**Final Report for AOARD Grant 104094, Study of Magnetocaloric Cooling for Thermal Management**

**November 12 2012**

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**Abstract:**

The work performed in the scope of this project deals with the investigation of the basic science aspects of magnetocaloric materials. Near room temperature magnetocaloric materials have attracted attention as a novel solid state cooling technology, with several advantages relative to conventional vapor compression systems. Interest in this field has dramatically increased due to high oil prices and the challenges of global warming. Some advantages of thermal management by magnetocaloric systems include: (a) solid magnetic material as a refrigerant, (b) no ozone depleting gases, (c) low noise and (d) high efficiency. Major companies, such as BASF, GE etc. have ongoing projects on magnetocaloric systems for industrial and residential applications. The materials system studied were Fe based and Heusler alloys, a magnetic refrigeration system was constructed and novel thermal management ideas suggested. Each of the projects was collaborative work, as stated in the results section. The magnetic properties of Co substituted Ni-Mn-Sn Heusler melt spun ribbons were investigated. DSC and VSM results show that the martensitic transition temperatures of Ni-Co-Mn-Sn decreased with increasing Co content. Co substitution resulted in a decrease in martensitic transition temperature by 25K per at. % Co. The

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14. ABSTRACT
**Near room temperature magnetocaloric materials have attracted attention as a novel solid state thermal management technology as it has several advantages over conventional vapor compression systems. This effort is an investigation of the basic science of magnetocaloric materials wherein Fe, Co-based and Heusler alloys were used as replacements for gadolinium alloys. Findings from differential scanning calorimetry (DSC) and vibrating sample magnetometry (VSM) of Co substituted Ni-Mn-Sn Heusler melt spun ribbons show that the martensitic transition temperatures of Ni-Co-Mn-Sn decreased with increasing Co content. Co substitution resulted in a decrease in martensitic transition temperature by 25K per at. %Co. The magnetocaloric effect (MCE) in Fe80-x B12Cr8REx (RE=La, Ce or Gd, x = 1-15%) alloys was also investigated. RE additions could be used to tune the Curie temperature (TC); TC could be adjusted near room temperature with relatively constant peak magnetic entropy change for Fe-B-Cr-Ce amorphous alloys. Construction of a magnetic cooling system was done which possessed an active magnetic double regenerator cycle (AM2RC) and control subsystems. An active transient cooling system was also developed.**

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magnetocaloric effect (MCE) in $Fe_{80-x}B_{12}Cr_8RE_x$ (RE=La, Ce or Gd, x = 1-15%) alloys was investigated. RE additions could be used to tune the Curie temperature ($T_C$). The $T_C$ was adjusted near room temperature with relatively constant peak magnetic entropy change for Fe-B-Cr-Ce amorphous alloys. The construction of a magnetic cooling system was performed which possessed an active magnetic double regenerator cycle (AM2RC) and control subsystems. An active transient cooling system was also developed.

**Introduction:**

The specific aim of this research is to study the basic science aspects of magnetocaloric materials. As stated by J.Y. Law (Ph.D. thesis, Nanyang Tech. Univ., Singapore 2011, PhD supervisor R.V. Ramanujan), "the magnetocaloric effect (MCE) describes the temperature change of a magnetic material induced by an adiabatic application or removal of an external magnetic field. This effect is particularly pronounced at temperatures and fields corresponding to magnetic phase transitions. This property can be employed in energy efficient refrigeration systems to reduce global energy consumption and the use of ozone depleting compounds, greenhouse gases and hazardous chemicals. The systems studied so far employ gadolinium alloys which are expensive, available in limited quantities and corrode easily. Development of new, cheap and corrosion-resistant magnetocaloric materials (MCM) are needed for most commercial applications." Hence, systems which were studied were chosen to be cheaper than Gd, such as Heusler alloys and Fe based alloys. We also constructed a magnetic cooling system and investigated thermal management systems. The importance of this work has been stated above and the ultimate future goal would be cheap, energy efficient, green magnetocaloric systems for thermal management.

**Experiment:** Description of the experiment(s)/theory and equipment or analyses.

The experimental details are fairly standard for the Heusler and Fe based alloys. The details are available in the relevant publications of Law et al. which are listed in the list of publications. In the case of the magnetic cooling system, the experimental description is fully described in earlier work by our collaborators, Liu and Zheng:

The construction is based on the previous work of Zheng et al, Intl. J. Refrigeration, 32, 78 (2009) and performed with B.H. Tan (graduate student), Drs Zheng and Prof Z.W. Liu. This design has been well received by the international community since excellent use is made of the magnetic field by the use of the **double** magnetocaloric system. A room temperature magnetic refrigerator consisting of permanent magnet, active magnetic refrigeration (AMR) cycle bed, pumps, hydraulic circuit, active magnetic double regenerator cycle (AM2RC) and control subsystems was developed. The magnetic field is supplied by NdFeB permanent magnets. The AMR bed, made of stainless steel 304, encloses the magnetocaloric working substance. Each part of the refrigerator is controlled by the programmable controller. Heat exchangers are employed to expel heat.

**b) Design of the experimental magnetic refrigerator**

The reciprocating refrigerator prototype is composed of magnetic field, hydraulic circuit, stainless steel AMR bed and control system. There are various sensors for measuring temperatures, pressures, flows, and electrical power. The schematic diagram of this magnetic refrigerator is shown in Fig. 1. There are eight electromagnetic valves to control the fluid direction, pumps, stepper motor, programmable controller (PLC) etc. In this system, PLC is the command center, which issues different orders according to the state of the permanent magnet indicated by the position switch.

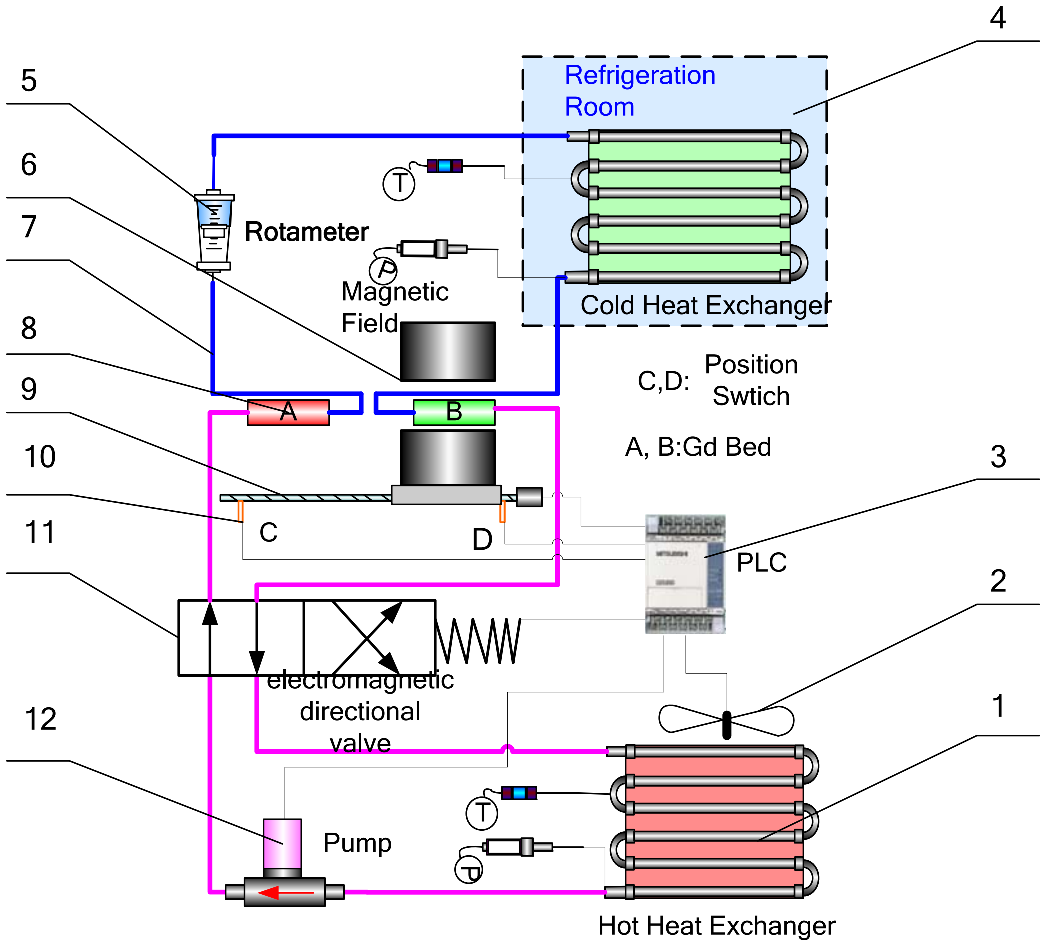



Fig.1 The Room temperature magnetic refrigerator (after Zheng et al)

1，4： radiator or replaced by Cu pipe 2

2：cooling fans 2

3: PLC (Program Logical Controller) parameter: 14 contact, 8 in, 6 out

5: flowmeter 1

6: permanent magnet 1, shown in Fig.2

7: water hope

8: magnetic refrigeration beds 2, shown in Fig.2

9: precision pattern assembly, including magnetic stepping motor, lead screw slipway,

controller of magnetic stepping motor

10: position switch 2

11: reversing solenoid valve

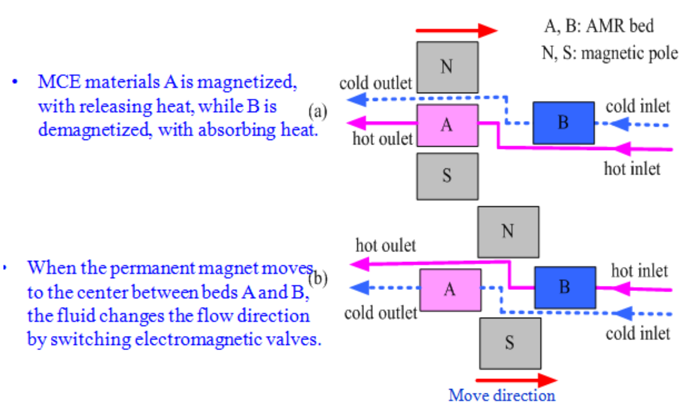
12: pump 0.8Mpa, 5L/min 1

13: bar clasps

14: DC power, 24V, 3A and 5V, 1A

**d) Design of AM2RC**

Two hydraulic circuits were used in this magnetic refrigerator. They perform the heat exchange for the hot heat circuit when magnetic refrigeration substance (MRS) is placed in the magnetic field and for the cold heat circuit when MRS is out of the magnetic field. Fig. 2 shows the structure of the AMR bed. The screens are fixed by frames and a bottom plate. The fluid flows through the magnetic materials continuously, and the heat transfer between the fluid and the materials occurs throughout the movement of magnet.



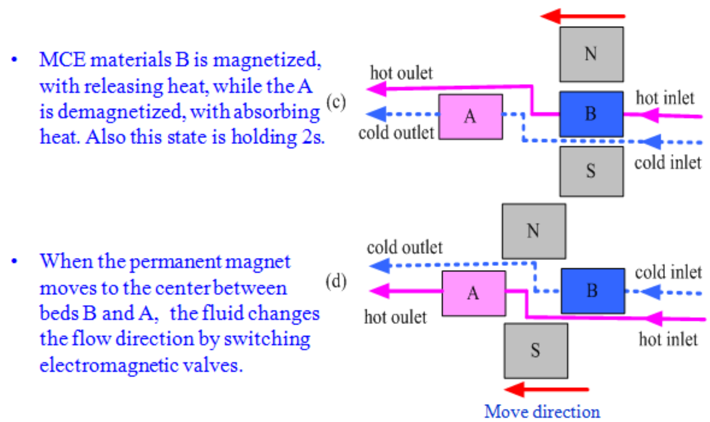



Fig. 2 AMR cycle (after Zheng et al)

To demonstrate active transient cooling of a heated electrical resistor by MCE, a proof-of-concept setup was designed and developed, as described in Active transient cooling by magnetocaloric materials, J. Y. Law, V. Franco (Universidad de Sevilla, Spain), P. Keblinski, R. V. Ramanujan, Applied Thermal Engg., accepted for publication, 2012.

The setup consists of a resistor (heater), Gd block, thermocouples and polystyrene insulation. The magnetic field was applied by an electromagnet, providing a maximum magnetic field of 16 kOe. Active cooling of thermal spikes using a benchmark MCE material (Gd) was investigated. To study conduction cooling by MCE, the resistor and Gd block were mounted in direct contact using nonmagnetic thermocouple wires to measure the time dependence of temperatures of the resistor, Gd and their interface. The influence of different heating power inputs of the resistor (1 W to 5 W) on the cooling behavior was studied.

**Results and Discussion:**

The results of the Heusler alloy work are ongoing. A manuscript: The Giant Magnetocaloric Effect in Co substituted Ni-Mn-Sn Heusler alloys is being prepared, with authors, X. Chen[1], V. B. Naik[2], A. Rebello[2], V. Suresh Kumar[2], R. Mahendiran[2], R. V. Ramanujan[1,*1]School of Materials Science and Engineering, Nanyang Technological University, Singapore 639798, Singapore.

[2]Department of Physics, National University of Singapore, 117542, Singapore. As mentioned earlier, the structure, martensitic transition and the magnetocaloric effect in Co substituted Ni-Mn-Sn Heusler melt spun ribbons were investigated. DSC and VSM results show that the martensitic transition temperatures of Ni-Co-Mn-Sn decreased with increasing Co content. Co substitution resulted in a decrease in martensitic transition temperature by 25K per at. % Co.

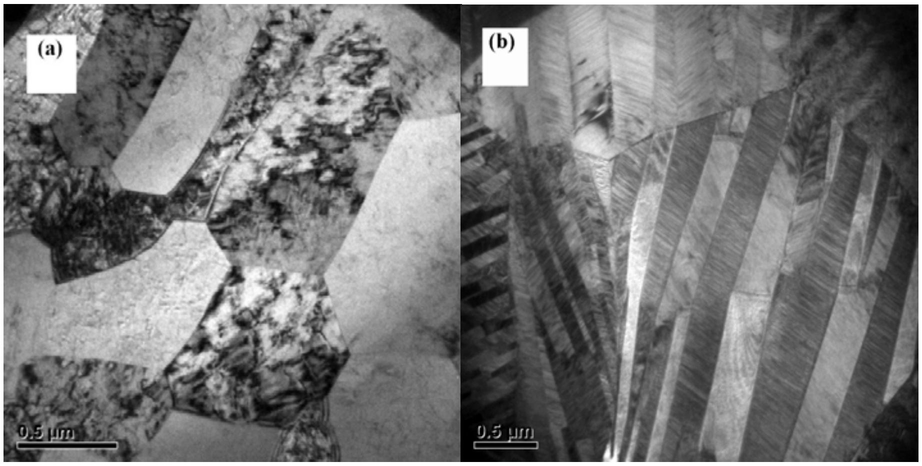



**Figure 2.** TEM analysis (a) BF micrograph of the Austenite phase in $Ni_{48}Co_2Mn_{38}Sn_{12}$. (b) Microstructure of platelike martensite.

This work is significant because it allows us to use affordable materials for magnetocaloric applications. Using magneto-structural transitions in these Heusler alloys will definitely broaden the range of materials available for this purpose, hence this work is significant.

<u>In the case of affordable Fe based alloys</u>, the work is well described in the following which is the abstract of the following paper: J.Y. Law, V. Franco and R.V. Ramanujan, Influence of La and Ce additions on the magnetocaloric effect of Fe-B-Cr based amorphous alloys, *Appl. Phys. Lett.*, 98, 192503 (2011). Again, the significance of the work is the possibility of using affordable magnetocaloric materials. The abstract is as follows:

**"Influence of La and Ce additions on the magnetocaloric effect of Fe–B–Cr-based amorphous alloys**


J. Y. Law,[1] V. Franco,[2] and R. V. Ramanujan[1,a]

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The magnetic entropy change __$S_M$_, temperature of peak _$S_M$ _$T_{pk}$_ and refrigerant capacity _RC_ in Fe_RE_$_{80}B_{12}Cr_8$ _RE=La, Ce, or Gd_ alloys were studied. Increasing La, Ce, and Gd content led to relatively constant, decrease, and increase in $T_{pk}$, respectively. Both the phenomenologically constructed universal curve for _$S_M$ and field dependence power laws demonstrated that these alloys exhibited similar critical exponents at Curie temperature. With 5% Ce added to $Fe_{80}B_{12}Cr_8$, $T_{pk}$ could be tuned near room temperature with relatively constant peak _$S_M$. $Fe_{79}B_{12}Cr_8La_1$ exhibited enhanced RC compared to $Gd_5Si_2Ge_{1.9}Fe_{0.1}$. The tunable $T_{pk}$ and enhanced RC are needed in active magnetic regenerators." Abstract of published paper. The key figures are also provided below.

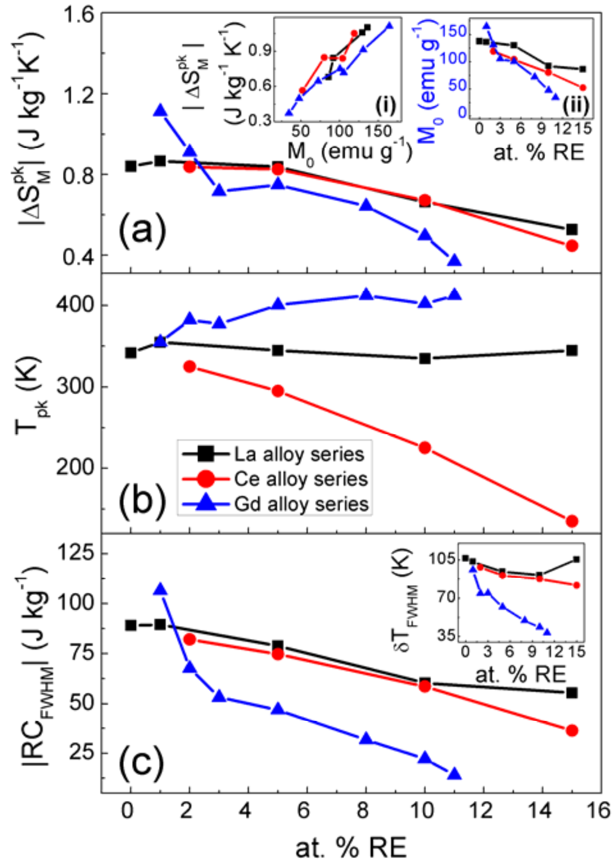


Fig. 3 Compositional dependence of (a) $\left|\Delta S_M^{pk}\right|$, (b) $T_{pk}$ and (c) $RC_{FWHM}$ for the as-spun ribbons at H = 11 kOe. 1a Inset: (i) Spontaneous magnetization dependence of $\left|\Delta S_M^{pk}\right|$ and (ii) Compositional dependence of $M_0$. 1c Inset: Compositional dependence of $\delta T_{FWHM}$. After Law et al

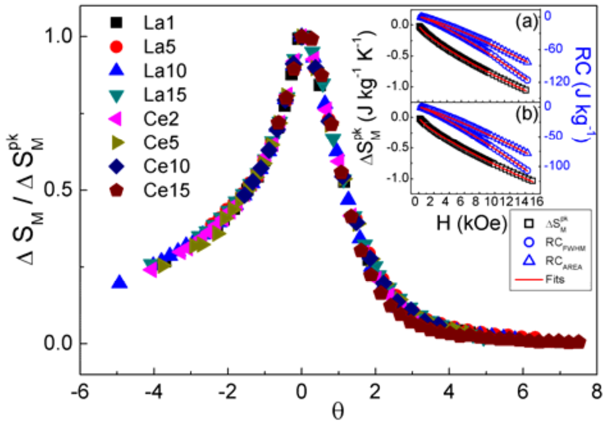


Fig. 4 Universal curves for $Fe_{80-x}B_{12}Cr_8RE_x$ where RE = La or Ce. Inset: Field dependence of peak magnetic entropy change and refrigerant capacity for (a) La5 and (b) Ce5 alloys. After Law et al

<u>In the case of the magnetic cooling system:</u>

Fig. 5 shows the actual experimental system constructed in NTU based on the ideas and design of Liu and Zheng who were our collaborators.

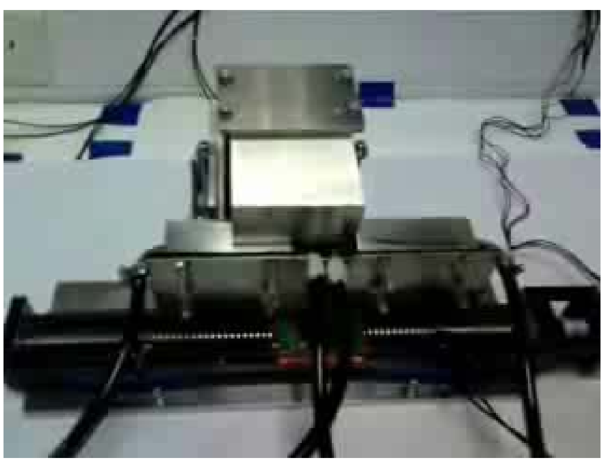

Fig. 5 Actual experimental system in NTU

This system was fabricated based on the above design, and tested, cooling of the heat transfer fluid was successfully obtained. However, due to the extensive corrosion of the Gd by the heat

transfer fluid, the experiment could not be continued. A thermodynamic analysis of the system revealed the previous results of Zheng et al, novel results were not obtained. The background to thermodynamic analysis of such systems can be found in the paper, Performance comparison of magnetic refrigeration cycles, F.C. Chen, G.L. Chen, R.W. Murphy and V.C. Mei, Cryocooler-6, Plymouth, Massachusetts, Oct25-26, 1990. In the work of Zheng et al, numerical analysis of the refrigeration cycle was performed. Using the Langevin theory of magnetism, the entropy change can be calculated for the case of Gd, which was used in the experiments. The Curie temp. and Lande factor are used as inputs. More details can be found in the original paper. The figure below from Zheng et al, shows the entropy change:

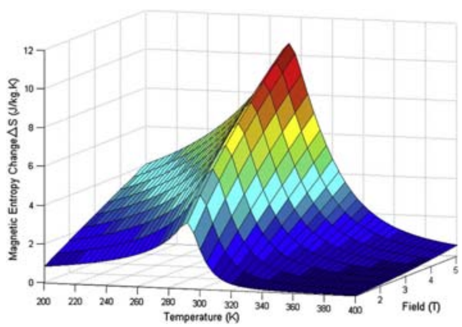


Fig. 6. Entropy change as a function of temp. and magnetic field (after Zheng et al)

It can be seen that the entropy change increases with magnetic field and peaks in the vicinity of the Curie temp. of Gd. The Ericsson cycle consists of 2 isothermal processes and two iso-field processes as shown in the figure below.

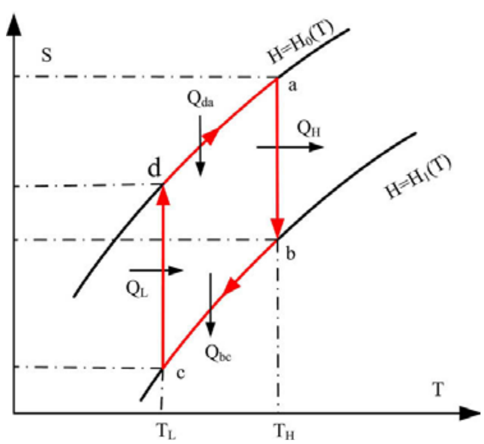


Fig. 7 Ericsson cycle schematic, after Zheng et al

The coefficient of performance (COP) can be calculated using the values of the entropy change and the heat capacities, including the magnetic heat capacity. It can be seen that COP decreases with increasing $T_{hot}$ and is higher at higher magnetic fields.

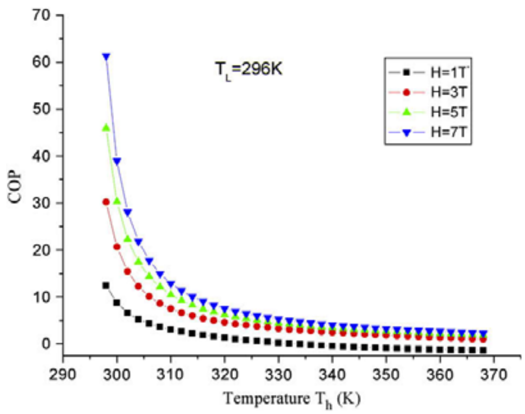


Fig. 8 COP v/s $T_{hot}$, $T_{low}$ = 296 K (after Zheng et al).

Finally, active transient cooling by magnetocaloric materials was studied, there is very little literature in this area, our collaborative paper has been accepted for publication in Appl. Thermal Engg. Below is the abstract:

**"Active transient cooling by magnetocaloric materials**


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Abstract:

The magnetocaloric effect (MCE) has been intensively studied for novel energy efficient thermal management systems. The present study demonstrates a proof-of-concept magnetic cooling setup for active cooling of the thermal spikes of a heated resistor. Using Gd as the MCE material, the device was capable of actively cool thermal spikes within one cycle since the dynamics of magnetic phase transition in Gd (a second-order magnetic phase transition material) are favorable to effect a fast MCE response. Enhanced cooling rate of the heated resistor of up to ~85% for active cooling by MCE compared to passive cooling was achieved. The cooling curve of the resistor was found to follow an exponential decrease. Our results show that magnetic cooling systems can be an efficient solution to cool thermal spikes in active transient cooling systems. Active cooling of thermal spikes of a resistor within one cycle using Gd as the magnetocaloric material was demonstrated.

- ~ 85 % faster cooling rate of the thermal spike of a resistor was achieved by active cooling by MCE compared to passive cooling for 1 W power heating.
- Our results show that MCE cooling can be an efficient solution to cool thermal spikes."

**List of Publications and Significant Collaborations that resulted from your AOARD supported project:**

*Peer reviewed journals and Ph.D. thesis*

J. Y. Law, V. Franco, P. Keblinski and R. V. Ramanujan, Active transient cooling by magnetocaloric materials, Appl. Thermal Engg., accepted for publication, 2012.

J. Y. Law, Ph.D. thesis, Nanyang Technological Univ., Singapore, 2011.

J.Y. Law, V. Franco and R.V. Ramanujan, Influence of La and Ce additions on the magnetocaloric effect of Fe-B-Cr based amorphous alloys, *Appl. Phys. Lett.*, 98, 192503 (2011).

J.Y. Law, R.V. Ramanujan and V. Franco, Tunable Curie temperatures in Gd alloyed Fe-B-Cr magnetocaloric materials, *J. Alloys Compounds*, 508, 14-19 (2010).

*Conference presentations*

R.V. Ramanujan, JY. Law and V. Franco, The magnetocaloric effect of Fe-B-Cr-Gd alloys, TMS Annual Meeting, USA (2011).

*Recognition*

Vice-Chair, Magnetic Materials Committee, TMS (USA) (since 2012).Lead Organizer, Invited Speaker, Magnetic Materials for Energy Applications -II Symposium, TMS Annual Meeting, USA (2012).

Invited Speaker, IEEE Magnetics Society Symposium, Singapore (2011).

Best Poster Award, S. Thomas, G. Pookat, S.S. Nair, M. Daniel, R.V. Ramanujan, M.R. Anantharaman and M. Albrecht, Nano 2011, Cochin, India (2011).

Plenary Presentation, Organizing Committee, Third International conference on Nanomaterials, Cochin (2011).

Judge, Magnetic Materials Symposium Poster Awards, International Conference n Materials for Advanced Technologies (ICMAT), Singapore (2011).

Session chair, Invited Speaker, Memory, nanomagnetics, materials and devices Symposium, International Conference on Materials for Advanced Technologies (ICMAT), Singapore (2011).

Fellow, American Society for Materials (2011)

Invited Speaker, IEEE Magnetics Society Symposium, Singapore (2011).

J.Y. Law, IEEE Magnetics Society (Singapore Chapter) Best Poster Award (2011).

J.Y. Law, IEEE Magnetics Society Summer School Scholarship (2011).

Executive Committee, IEEE (Magnetics Society), Singapore Chapter (2011).

Invited Presentation, Nucleation in magnetic nanomaterials, Conf. organized by US Air Force Research Labs, USA (2010).